DEVELOPMENT OF A SAMPLING TECHNIQUE TO CONCENTRATE PICOGRAM AMOUNTS OF RADIOACTIVE AND NON RADIOACTIVE METALS FROM LARGE VOLUMES OF WATER

--PROJECT REPORT--

PREPARED

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EXECUTIVE SUMMARY

Laboratory and field studies have been carried out to evaluate a filter device to concentrate program amounts of radioactive and non-radioactive elements from 20 litre volumes of water. The best device was found to be comprised of manganese dioxide impregnated onto acrylic fibre and packed into filter cassettes.

The results of the laboratory studies showed that, of the elements studied, only the concentrating of radium-226 is relatively unaffected by the solution pH, between 3 and 9, solution hardness, between 0 and 1,000 mg/L $CaCO_3$, and solution temperature, between 10 and 20 degrees celsius. In all of the laboratory experiments, the efficiency of the device for radium-226 was greater than 90% while its capacity exceeded 100 bequerel.

The results of the field study gave indication that the manganese dioxide filtering device concentrates only the "dissolved" radium-226 and is ineffective as a means of concentrating the "undissolved" portion. This characteristic is particularly attractive to regulatory agencies whose main concern is "dissolved" concentrations rather than "total". Further field work is needed to confirm and document these observations.

The manganese dioxide concentrating device is proposed to have very good possibility as a Canadian vehicle to export radio-analytical services. Advantages such as increased sensitivity, lower analysis costs and increased ease of sampling are cited as its main characteristics.

While not formally measured, there is no reason to believe that the attractiveness of the manganese device for radium-228, radium-224 and radium-223 will be different in any way from its attractiveness for radium-226. This is an additional feature of the device.

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1 - INTRODUCTION

The determination of sub-parts per billion (ug/L) concentration levels of naturally occurring radionuclides and man-made nuclear fission products in Canadian water often requires lengthy analytical procedures, large sample volumes and/or costly and sophisticated analytical instrumentation. These often impose capital and manpower restrictions on government and private sector laboratories. In addition to the logistics of transportation, the large sample volume requirements (10-20 litres) can severely limit the speed and magnitude of environmental assessments. The fact that each sample must be appropriately preserved in the field, with acid, serves to compound the difficulties and introduce safety concern.

To reduce the analytical limitations of measuring trace levels of radioactive elements in water, it is desirable to develop and evaluate a light weight, portable sampling technique that will allow the field environmentalist to rapidly and accurately concentrate the elements of interest. Such a technique would offer several features: (1) the weight of each sample, sent to the laboratory for analysis, would be reduced by two or three orders of magnitude (20 gm versus 20 kg); (2) the shipment time would be reduced (airmail versus land transportation); (3) larger samples than would normally be collected could be subjected to pre-concentration in the field while not increasing shipping weight and costs; (4) it would not be necessary to transport corrosive and dangerous preserving acids to remote sampling locations. This would be particularly desirable where air transportation is the only mode of transportation; (5) storage space, while the water samples are awaiting analysis, would no longer be a consideration; (6) sample spillage during shipment would no longer be a concern.

Several modes of sample concentration have been discussed in the literature. Roy et al. (1,2) have shown that the alum sludge from water treatment facilities is a good media for concentrating radionuclides from large volumes of water. Durham and Joshi (3) have also applied this technique to the determination of radioactive species in Lake Ontario. One of its major limitations is that the acquired sample represents integration over a long period of time rather than an instantaneous "grab" sample. Also,very few sample sites have water treatment facilities. A modification of this water concentration scheme has been described by Wong et al (4).

These workers coprecipitated, along with manganese dioxide, cations from 50 to 400 liters of an aqueous grab sample. The precipitate was then isolated by filtration and sent to the laboratory for determination of the coprecipitated elements. As a routine field concentration technique, both of these batch procedures have the disadvantage that cumbersome processing and filtration equipment is needed.

1.1 Manganese Dioxide as a Concentration Media

The earliest published references to the ability of certain forms of manganese dioxide to adsorb radium date back to the early years of the century. Ebler (5) reported high levels of radium in the sediments of the Baden-Baden thermal springs in Germany. These sediments contained a mineral called "Reissacherit" which contains hydrated manganese dioxide. The phenomenum is also observed in the nearby Bad-Gastein area of Austria where the air over the thermal springs contains high levels of radon (~75 Bq/L). The water contains negligible levels of radium (~0.048q/L) but the manganese sediment may have as much as 17000 Bq/g (6). It is also significant that some natural forms of manganese dioxide are minerals which contain radium such as Hollanderite and Psilomelane. Recently,high resolution electron microscopy of such materials (7) revealed that the manganese dioxide tetrahedral crystals arrange themselves to form a tunnel in which heavy cations of specified ionic radius can be accommodated. It is not clear whether this behaviour is the cause of, or the effect of, the affinity of the molecule for radium, barium and other heavy metals.

The attributes of the minerals in the thermal springs of Bavaria were reproduced in the laboratory by Ebler and Bender (1913). These workers added methanol to potassium permanganate to produce a dense brown sludge. This brown sludge was found to adsorb radium in preference to barium and seemed to be a promising method for purifying radium from barium salts. (A problem of some importance at that time when radium was widely used for medical treatment). The work was interrupted during World War I and according to the available literature, not continued afterwards.

Interest in manganese dioxide as a method for collecting dissolved radioactivity has been revived in recent years. It was in the field of oceanography that the material found new application. The distribution of radioactive trace elements is of prime importance in the study of geochemical tracers, particularly in the understanding of sedimentation in the ocean. Radium-228, with a half - life of 6.7 years, is a particularly useful isotope for the study of absorption of elements from sea-water by ocean sediments and marine organisms. The isotope has an activity concentration in sea-water of only 10-4 Bq/L and thus several hundred litres are required per sample, if the radium-228 is analysed directly. Obviously, any method of preconcentrating the activity will eliminate the need to collect and process huge quantities of sea-water. It is known that ferric hydroxide is an excellent scavenger of certain trace metals. Thus in the late 60's Indian scientists in collaboration with the Scripp's Institution of Oceanography experimented with natural sponges and jute impregnated with ferric hydroxide. It was found that 1 kg of this material would adsorb the activity of several hundred litres of surrounding sea-water . Further improvements were made (8) by substituting synthetic acrylic fibre for the natural sponge and jute. With iron impregnated fibre concentration factors (defined as number of litres of dissolved activity adsorbed per kg) of 10,000 were reached for Th-234 and Pb-210. However, the factor for radium, was not so high , being only in the range of 500.

In the early 70's, W.S.Moore suggested that the acrylic fibre be impregnated with manganese dioxide rather than ferric hydroxide. His "magic fibre" was originally prepared (9) by immersing acrylic fibre in a strong NaOH solution. This resulted in the white fibre turning red and being converted to an ion-exchange medium. The converted fibre was then immersed in a solution of MnC12 to form the finished , black coloured , product . This original recipe produced a fibre which contained a fair amount of loose powder. Some of the fibre was grey or off-white indicating that portions are not effectively converted. This fibre has been used by the oceanography group at Texas A & M University for many studies in the Gulf of Mexico. One of the first inland applications (10) of the fibre was to remove radium from artesan wells in Texas an area where extensive uranium deposits give rise to high levels in natural waters.

A newer method of preparing fibre , also described by Moore (11), results in a much cleaner jet-black finished product, having excellent characteristics for the adsorption of radium, thorium and lead. In this method, fibre after washing and combing, is immersed in potassium permanganate solution. Obviously the reaction that occurs is similar to the oxidation of methanol described above.

Interest in the affinity of radionuclides for naturally occurring manganese minerals has been revived by the discovery that nuclides in U.S. radioactive waste disposal sites are found to concentrate in areas having the highest concentration of manganese in the geological formation. So strong is this correlation, that it has been proposed to mix manganese dioxide in with nuclear waste to prevent migration (12).

Moore reported that lead, mercury, copper, zinc, cobalt, cadmium, plutonium, thorium and radioactive species such as americium-241, europium-155, antimony-125, bismuth-207, ribidium-86, rhodium-106, were also adsorbed on manganese dioxide.

II - LABORATORY PROGRAM OBJECTIVES

The prime objective is to devise and evaluate a water sampling device containing manganese dioxide impregnated on a suitable substrate. Manganese dioxide has been shown in the literature to possess a strong affinity for radium-226 and there is suggestions that it also has a strong affinity for heavy metals such as lead, mercury, copper, zinc, cobalt, cadmium, plutonium, thorium, etc. A definite advantage of such a device ,relative to an ion exchange resin is that it would possess a very low affinity for calcium, magnesium, sodium and potassium, the major cations in ground waters and surface waters.

The characteristics of the sampling device are that it should be light in weight, small in size, easily prepared and inexpensive in cost.

The first phase of the project was to carry out evaluations and testing in the laboratory. The second phase was to be a field demonstration of its applicability.

The Phase I laboratory work is divided into six tasks, A to F. The description of each, as described in the unsolicited proposal, was as follows:

TASK A

The first task is to evaluate several substrates for ease of impregnation with MnO2. There is indication from previous work carried out for Environment Canada and Eldorado Resources Ltd.(14) that the efficiency and capacity of the MnO2 filter for radium-226 is influenced by the nature of the support medium. Four substrates; glass wool, cellulose fiber, shreaded nylon and wood chips are to be impregnated with manganese dioxide. Each is to be packed into 10 cm by 1 cm tubes and a known volume of solution , containing known concentrations of thorium-228, radium-226, lead-210, mercury, cadmium, cobalt, selenium, and uranium , passed through each. The effluents are to be collected and analysed by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and standard radiochemical procedures (13). The removal efficiency of the filter for each cation is to be determined as a function of the amount adsorbed. It is also proposed that the capacity of each filter is to be determined by passing the solution through the filter and monitoring the effluent concentrations until adsorption ceases.

TASK B

Using the optimum filter, chosen from Task A, the effects of the variables pH, solution temperature and water hardness on efficiency and capacity are to be determined. Temperatures of 5+/-2 degrees C and 24+/-3 degrees C; pH values of 4.0 and 9.0; hardness of 200 and 1000 mg/L CaCO3 were the variables that were suggested. The same solutions used in Task A are to be used to carry out this task.

TASK C

Evaluate two sample schemes from the point of view of practicality and durability. One is to be gravity fed and the other is to be pump fed. The standard solution temperature of 24 degrees C was suggested and the effluent is to be analysed as a function of time.

TASK D

To measure the influence of sample flow rate on the recovery effectiveness of the apparatus. Flow rates of 1 litre per minute and 10 litres per minute were suggested.

TASK E

Six filters from the above Tasks A to D are to be choosen for this task. The adsorbed elements are to be desorbed by two techniques; nitric acid wash and hydroxylamine hydrochloride wash(3 filters each). The resulting solutions are to be analysed to evaluate the use of the filters as an analytical sampling media.

TASK F

The influence of dissolved iron on the removal efficiency of the manganese dioxide filter for radium-226 is to be investigated.

III - EXPERIMENTAL PROCEDURES AND RESULTS

3.1 Procedure for Filter Media Preparation

All manganese impregnated filter media were prepared by immersion of the substrate in 0.4M potassium permanganate for 2 days at 70- 80 degrees Celsius. The resulting black/brown coloured media were then washed for 10 to 15 minutes with deionized water. For evaluation purposes the media was packed into nucleopore cassettes. A photograph of the device is shown below.

3.2 Analytical Methodologies

Cadmium, cobalt, selenium and uranium in the eluants, were determined by Inductively Coupled Plasma Emission Spectrometry (ICP-ES). Mercury was determined using long path length UV spectrophotometry. The radioisotopes, radium-226, and thorium-228 were determined by alpha spectrometry (13) while the lead-210 wasdetermined indirectly by beta counting of its immediate daughter bismuth-210 (13).

Photo 1. Manganese Dioxide impregnated media and holder.

3.3 Results

3.3.1 Determine the Most Effective Substrate

In addition to glass wool, wood chips, shredded nylon and cellulose fiber, attempts were made to coat three additional substrate materials with manganese dioxide. They were acrylic fibre, ABS pellets and silica gel. Conclusions regarding success were based on visual observation. The results are as follows:

SUBSTRATE	APPARENT ATTRACTIVENESS FOR MnO2
1. Hardwood Chips (1-2 mm, dry)	Very good
2. Glass wool	Poor
3. Polypropylene air filter	Poor
4. Cotton batting	Good (but disintegrates)
5. Cotton fabric (non woven) filter	Fair
6. ABS pellets	Good
7. Silica Gel	Very good
8. "CUNO" 50 micron acrylic/phenol resin filter (after crushing in blender)	Good
9. "Thinsulate" (basically nylon)	Fair
10. Polyester fibre	Poor

From these ten coated substrates it was decided that the ABS pellets, the silica gel, the hardwood chips and the acrylic resin based media were the most promising. Each of the packings were washed thoroughly with deionized water and loaded into three piece, Nucleopore cassettes (no. 300045 , 33.5 mm id by 85 mm high, 45 millilitre volume, see photograph 1). These holders were choosen for testing because they were a definite improvement over the original proposal to use 10 cm by 1 cm tubes. In addition to their larger capacity for the filter media they were found to seal better, to possess more standard bore openings and hence more compatability with plastic tubing usually found in a laboratory.

A test solution containing approximately 3 Bq/L Ra-226, 3 Bq/L Th-228, 4 Bq/L Pb-210, 2 mg/L U, 1 mg/L Cd, 1 mg/L Co, 1 mg/L Se and 0.1 mg/L Hg was prepared. Twenty litre portions of this solution were passed through each of the cassettes containing the four different packings. The effluents from each were collected at regular intervals., in 1 litre containers and submitted for analysis. The radioisotopes, Ra-226, Th-228 and Pb-210 activities were measured in the 1, 5, 10, 15 and 20 litre samples, while the 5, 10, 15 and 20 litre samples were analysed for the other elements. The results obtained are tabulated in Table 1. Figure 1 is a plot of removal efficiencies of each filter as a function of volume and identity of cation eluted.

The data in Figure 1 show that, for Cd, Co, Se, U, and Hg, all four of the manganese filters gave recoveries of less than 50%. For the radionuclides the results were dramatically different. The acrylic fiber coated materials showed recoveries of greater than 90% for Ra-226 and Pb-210 and greater than 70% for Th-228. The three other filters, i.e., manganese dioxide deposited on wood chips, manganese dioxide deposited on ABS pellets and manganese dioxide deposited on silica gel, showed fluctuating recoveries that were less than 75% in all cases. The acrylic fiber/MnO2 filter was further evaluated by passing an additional 40 litres of solution through it. The objective was to determine the capacity of the filter for Ra-226, Th-228 and Pb-210. The results, included in Table 1, revealed that the removal efficiency did not deteriorate and the capacity for these isotopes is greater then 120 Bq. Further experimentation is necessary in order to precisely determine its capacity.

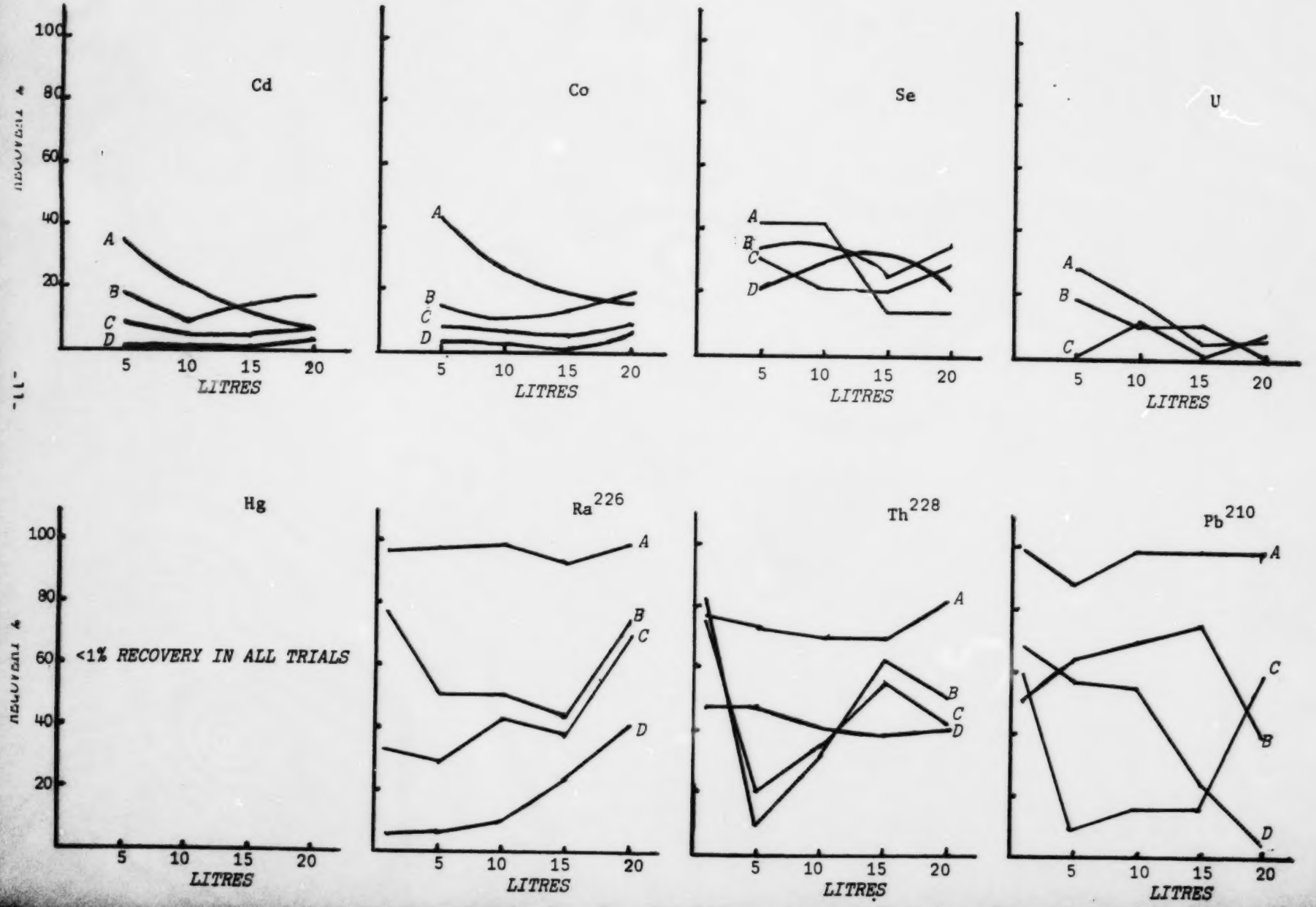
As a result of the experimentation carried out under Task A, it is concluded that the most effective filter for removal of Ra-226, Th-228, and Pb-210 from solution (under the conditions of pH, flow rate and temperature used) is acrylic fiber coated with manganese dioxide. Its efficiency of removal and capacity for those radionuclides suggests that it is ideally suited for sampling natural surface or ground waters. On the other hand , the data, presented here did not show good removal efficiency for Cd, Co, Mn, Se, U, or, at least, not at a pH of 2.7.

TABLE 1 EFFECTIVENESS OF METAL REMOVAL BY MANGANESE DIOXIDE AS A FUNCTION OF FILTER SUBSTRATE

Flow Rates for Acrylic Fibre, 470 mL/min; for Wood, 590 mL/min; for ABS, 600 mL/min; for Silica Gel, 625 mL/min; pH = 2.7, T = 18°C. Numbers in brackets refer to removal efficiencies in terms of percent.

Substrate	Elution Volume, Litre	Cd mg/L	Co mg/L	Mn mg/L	Se mg/L	U mg/L	Hg mg/L	Ra-226 BQ/L	Th-228 BQ/L	Pb-210 BQ/L
	Starting Sol'n	1.17±0.03	0.98±0.03	≤0.001	1.4±0.1	1.48±0.06	0.085	3.13±0.13	3.37±0.05	4.4±0.3
Acrylic Fibre	1	---	---	---	---	---	---	0.09±0.03 (97)	0.79±0.06 (77)	≤0.05 (≥99)
	5	0.76 (35)	0.56 (43)	0.97	0.82 (42)	1.06 (28)	0.089 (0)	0.06±0.02 (98)	0.91±0.06 (73)	0.54±0.06 (88)
	10	0.92 (21)	0.72 (27)	0.58	0.81 (42)	1.21 (18)	0.089 (0)	≤0.05 (≥99)	1.0 ±0.1 (70)	≤0.05 (≥99)
	15	1.03 (12)	0.79 (19)	0.47	1.2 (14)	1.41 (5)	0.084 (0)	0.20±0.06 (94)	1.02±0.07 (70)	≤0.05 (≥99)
	20	1.09 (7)	0.82 (16)	0.47	1.2 (14)	1.39 (6)	0.081 (0)	≤0.05 (≥99)	0.62±0.06 (82)	≤0.05 (≥99)
	30	---	---	---	---	---	0.089 (0)	0.25±0.02 (92)	0.84±0.02 (75)	≤0.05 (≥99)
	39	---	---	---	---	---	0.088 (0)	0.15±0.04 (95)	0.53±0.08 (84)	0.16±0.02 (96)
Wood	1	---	---	---	---	---		0.73±0.03 (71)	0.79±0.06 (77)	2.2±0.2 (50)
	5	0.96 (18)	0.83 (15)	5.1	0.93 (34)	1.20 (19)	0.087 (0)	1.52±0.11 (51)	2.66±0.14 (21)	1.6±0.1 (64)
	10	1.07 (5)	0.88 (10)	7.1	0.9 (35)	1.33 (10)	0.084 (1)	1.53±0.10 (51)	2.19±0.13 (35)	1.3±0.1 (70)
	15	0.99 (15)	0.86 (12)	6.8	1.05 (25)	1.31 (11)	0.084 (1)	1.74±0.10 (44)	1.49±0.07 (56)	1.1±0.1 (75)
	20	0.96 (18)	0.80 (18)	7.8	0.91 (35)	1.47 (1)	0.084 (1)	0.79±0.09 (75)	1.97±0.12 (42)	2.7±0.2 (39)
ABS	1	---	---	---	---	---		2.93±0.14 (6)	0.59±0.05 (82)	1.8±0.2 (59)
	5	1.07 (9)	0.90 (8)	0.01	0.96 (31)	1.46 (1)	0.084 (1)	2.90±0.16 (7)	3.04±0.15 (10)	4.0±0.3 (9)
	10	1.11 (5)	0.91 (7)	0.008	1.1 (21)	1.30 (12)	0.084 (1)	2.83±0.18 (10)	2.29±0.13 (32)	3.7±0.3 (16)
	15	1.10 (6)	0.93 (5)	0.007	1.1 (21)	1.53 (0)	0.084 (1)	2.40±0.06 (23)	1.24±0.08 (63)	3.7±0.3 (16)
	20	1.10 (6)	0.89 (9)	0.017	1.0 (29)	1.34 (9)	0.084 (1)	1.86±0.04 (41)	1.64±0.09 (51)	1.8±0.2 (59)
Silica Gel	1	---	---	---	---	---		2.06±0.12 (34)	1.78±0.04 (47)	1.4±0.1 (68)
	5	1.16 (1)	0.95 (3)	≤0.001	1.1 (21)	1.57 (0)	0.083 (2)	2.23±0.14 (29)	1.80±0.03 (47)	1.9±0.2 (57)
	10	1.17 (0)	0.95 (3)	≤0.001	1.0 (29)	1.49 (0)	0.084 (1)	1.78±0.14 (43)	2.01±0.13 (40)	2.0±0.2 (55)
	15	1.17 (0)	1.00 (0)	≤0.001	0.95 (32)	1.53 (0)	0.084 (1)	1.93±0.13 (38)	2.09±0.14 (38)	3.3±0.3 (25)
	20	1.12 (4)	0.90 (8)	0.002	1.1 (21)	1.36 (8)	0.084 (1)	0.97±0.08 (69)	2.00±0.10 (41)	4.2±0.3 (5)

FIGURE 1 - Removal Efficiencies as a Function of Filter Substrate
A, acrylic; B, wood; C, ABS; D, silica gel; pH=2.7, Hardness=0 mg/L $CaCO_3$



3.3.2 Task B - (1) Influence of pH on Recovery Efficiency of The Acrylic Fibre/Manganese Dioxide Filter

The behaviour of the Cd, Co, Se, U, Hg, Ra-226, Th-228, Pb-210 at pH 2.7 is illustrated in Table 1. Table 2 shows the removal efficiency of the acrylic fibre/manganese dioxide filter for Cd, Co, Se, U, Hg, Ra-226, Th-228 and Pb-210 at pH values of 3.0, 4.0, 5.0 and 7.0. This data, in addition to the pH 2.7 data, is plotted in Figure 2 as a function of removal efficiency versus total weight (or activity) of the element eluted through the filter.

Several observations can be made:

1. For Cd, Co, and Hg, the removal efficiency is greater than 80% when the pH is >3.0. At pH 2.7 the efficiency was dramatically poorer.

2. The removal efficiency of Th-228 and Pb-210 as a function of pH appears to be opposite to that of Cd, Co and Hg. That is, the highest efficiency (70%) was observed at pH 2.7 but decreased dramatically as the pH increased until a minimum efficiency (<10%) was noted about pH 4. At pH 7 the removal efficiency of the filter increased to40%.

3. The removal efficiency for the filter for Ra-226 is excellent at all pH levels from 2.7 to 7.0. In all cases the recoveries were greater than 90% and the capacity of the filter for the isotope was more than 100 Bq.

(2) Influence of Solution Hardness on the Recovery Efficiency of the Acrylic Fibre/Manganese Dioxide Filter

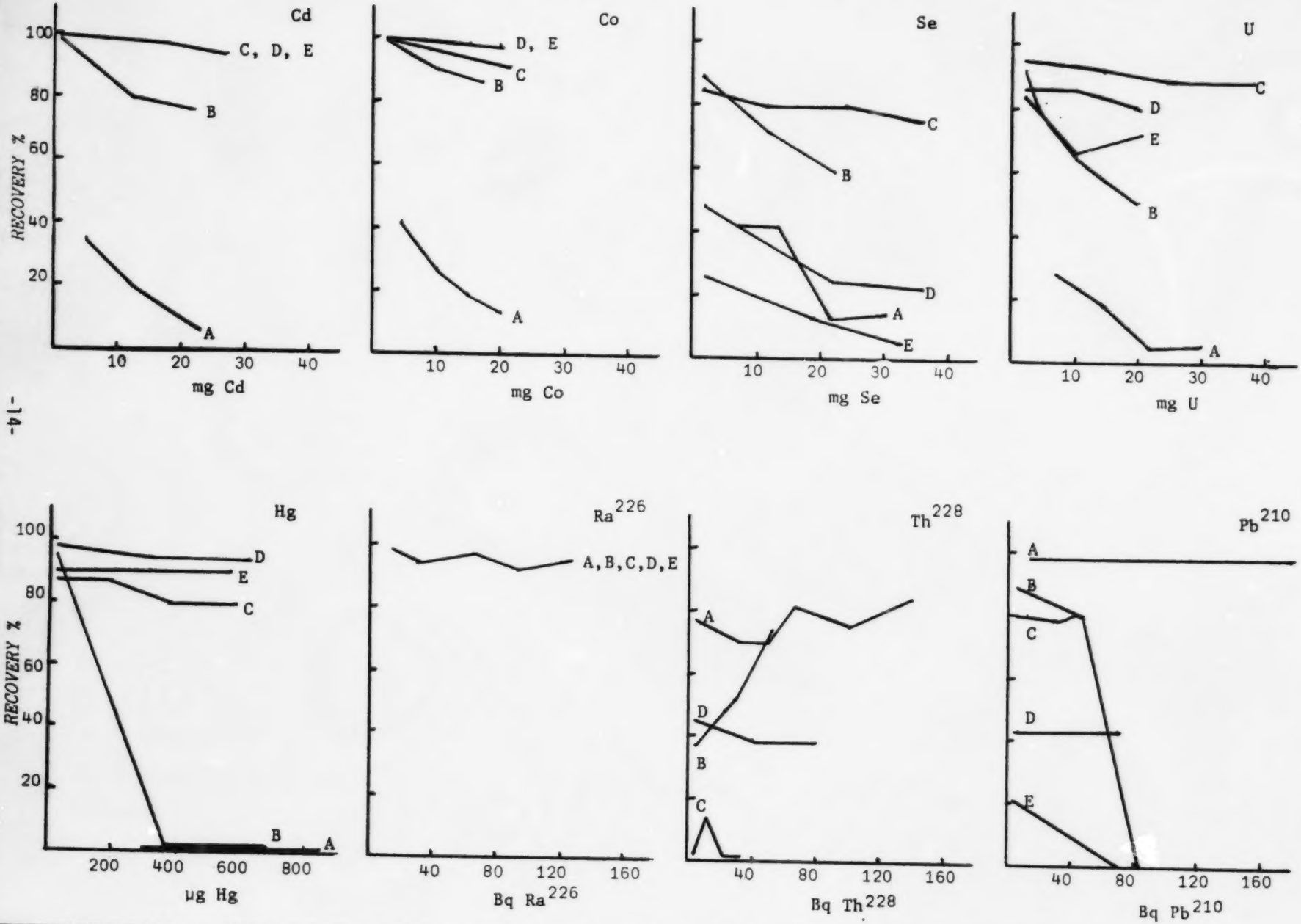
The filter was evaluated at hardness values of 200 mg/L and 1000 mg/L CaCO3 for two pH values of 4.0 and 9.0. The results are shown in Table 3. The data are illustrated in Figures 3 and 4 where removal efficiency is plotted against total weight (or activity) of the element eluted through the filter.

TABLE 2 INFLUENCE OF pH ON REMOVAL EFFICIENCY OF MANGANESE DIOXIDE/ACRYLIC FIBRE FILTER
flow = 0.4 L/min, hardness = 0 mg $CaCO_3$/L

pH	Elution Volume, Litre	Cd mg/L	Co mg/L	Se mg/L	U mg/L	Hg mg/L	Ra-226 Bq/L	Th-228 Bq/L	Pb-210 Bq/L
3.0	Start	1.22	0.97	2.0	1.41	0.038	7.8 ±0.4	3.00±0.12	4.7 ±0.2
	1	0.02 (98)	≤0.01 (99)	0.22 (89)	0.1 (>93)	0.002 (95)	0.11±0.04 (99)	1.80±0.09 (37)	0.50±0.05 (89)
	10	0.24 (80)	0.10 (90)	0.57 (72)	0.49 (65)	0.045 (0)	0.06±0.04 (99)	1.45±0.11 (52)	0.64±0.06 (80)
	18	0.29 (76)	0.13 (87)	0.82 (59)	0.69 (51)	0.039 (0)	0.05±0.03 (99)	0.79±0.07 (74)	6.0 ±0.03 (0)
4.0	Start	1.48	1.27	2.0	2.12	0.031	9.3 ±0.3	1.82±0.17	2.2 ±0.1
	1	0.01 (99)	0.01 (99)	0.30 (85)	≤0.10 (95)	0.004 (87)	0.30±0.06 (97)	1.81±0.19 (1)	
	2	-	-	-	-	-	-	-	0.44±0.04 (80)
	5	-	-	-	-	-	-	-	≤0.3 (86)
	6	0.03 (98)	0.04 (97)	0.40 (80)	0.14 (93)	0.004 (87)	0.20±0.02 (98)	1.54±0.14 (15)	-
	9	-	-	-	-	-	-	-	≤0.3 (≥86)
	12	0.05 (97)	0.09 (93)	0.40 (80)	0.23 (89)	0.006 (80)	0.25±0.07 (97)	1.8 ±0.2 (1)	-
	13	-	-	-	-	-	-	-	0.49±0.05 (78)
	17	-	-	-	-	-	-	-	0.45±0.05 (80)
	18	0.09 (94)	0.12 (91)	0.50 (75)	0.24 (89)	0.006 (80)	0.30±0.06 (97)	1.8 ±0.2 (1)	
5.0	Start	1.26	0.97	2.11	0.75	0.034	7.7 ±0.4	4.47±0.13	3.5 ±0.2
	1	0.02 (98)	≤0.01 (99)	1.09 (48)	0.1 (>87)	0.001 (97)	0.34±0.06 (96)	2.45±0.13 (45)	2.0 ±0.1 (43)
	10	0.03 (98)	≤0.01 (99)	1.56 (26)	0.1 (>87)	0.002 (94)	0.13±0.04 (99)	2.77±0.11 (38)	2.0 ±0.1 (43)
	18	0.04 (97)	≤0.01 (99)	1.65 (22)	0.15 (>80)	0.002 (94)	0.06±0.03 (99)	2.77±0.11 (38)	2.0 ±0.1 (43)
7.0	Start	1.12	0.07	1.86	0.71	0.031	6.1 ±0.4		3.9 ±0.2
	1	0.02 (98)	≤0.01 (99)	1.37 (26)	0.1 (>86)	0.003 (90)	0.40±0.2 (94)		3.1 ±0.2 (21)
	10	0.05 (96)	≤0.01 (99)	1.62 (13)	0.25 (65)	0.003 (90)	0.36±0.2 (94)		3.5 ±0.2 (10)
	18	0.05 (96)	≤0.01 (99)	1.76 (5)	0.20 (72)	0.003 (90)	0.48±0.3 (97)		4.8 ±0.2 (0)

FIGURE 2 - Recovery Efficiency of MnO_2/Acrylic Filter as a Function of pH.

Hardness=0 mg $CaCO_3$/L. A, pH 2.7; B, pH 3.0; C, pH 4.0; D, pH 5.0; E, pH 7.0. Solution Temp = 19°C.



At pH 4.0, Figure 3 shows that for Cd, Co, and U the recovery efficiency decreased as the hardness increased. For example with Cd the maximum efficiency was >90% at zero mg/L CaCO3 hardness and decreased to ~50% and ~30% at 200 mg/L and 1000 mg/L, respectively. For Hg the recovery efficiency was >80% at zero hardness but decreased to <10% at hardness of 200 and 1000 mg/L CaCO3. The results for Se were slightly ambiguous in that the recovery at 200 mg/L CaCO3 hardness was 40% but was much poorer at zero and 1000 mg/L hardness. At this pH ,Th-228 was recovered to less than 40% at all three hardness levels. Lead-210 recoveries approached 100% at all three levels while Ra-226 was greater than 95% at 0 and 200 mg/L CaCO3 but decreased slightly to 80% at 1000 mg/L CaCO3(temperature 9 degrees celsius).

Figure 4 shows that at pH 9.0, the influence of hardness on Cd and Co removal efficiency is much lower than at pH 4.0. For example at pH 4.0 the removal efficiency decreased by more than 30% (absolute) when the hardness was increased from 200 to 1000 mg/L. At pH 9.0 that decrease was 20% (absolute). For Co the increase in hardness, from 200 to 1000 mg/L, decreased the recovery by only 10% (absolute) while at pH 4 a decrease in recovery of approximately 25% was noted. The behaviour of the filter toward uranium at this pH was not able to be measured because of solubility considerations, i.e., precipitation occured. For Ra-226 the influence of a hardness increase to 1000 was negligible with >90% recovery observed at 200 and 1000 mg/L CaCO3. As at pH 4 , the recoveries for Pb-210 was independent of hardness and approached 100%. The behaviour of the filter toward Th-228 at pH 9 and hardness of 200 and 1000 mg/L CaCO3 was observed to be identical with removal efficiencies of greater than 90% noted at both hardnesses.

(3)Influence of Solution Temperature on Removal Efficiency.

The experiments whose data is reported in Table 3 were repeated at a somewhat lower temperature and reported in Table 4 . They are also illustrated in Figures 3 and 4, along with the 19 degree Celsius data. Generally speaking, for all the elements evaluated, the ten degree celsius difference in solution temperature had very little influence on the MnO2 filter performance.

FIGURE 3 - Influence of Solution Hardness (H) and Temperature On Recovery Efficiency of MnO_2/ Acrylic Fibre Filter at a pH of 4. A, H=0; B, H=200 mg/L $CaCO_3$; C, H=1,000 mg/L $CaCO_3$.

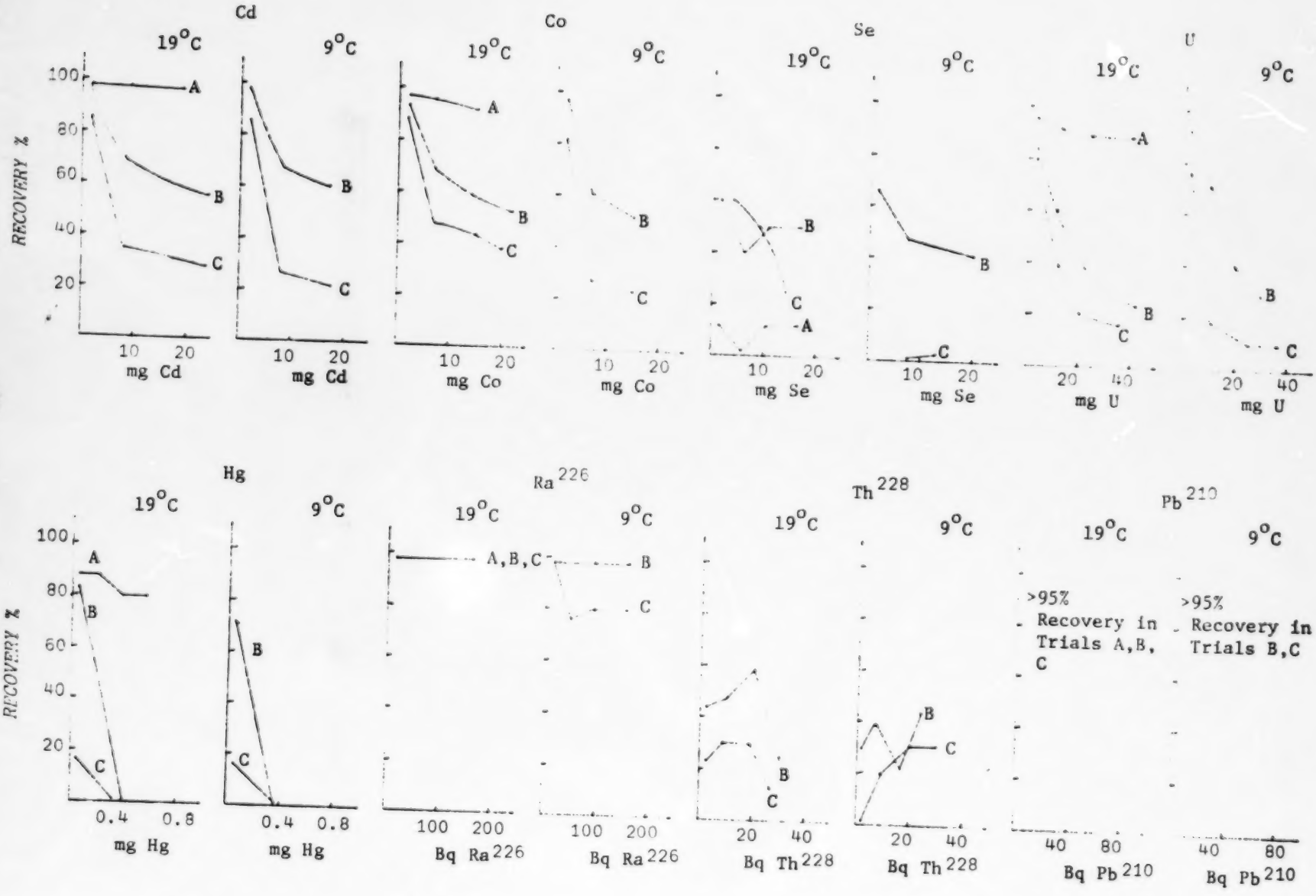


FIGURE 4 - Influence of Solution Hardness (H) and Temperature on Recovery Efficiency of MnO_2/Acrylic Fibre Filter at a pH of 9.

B, H=200 mg/L $CaCO_3$; C, H=1000 mg/L $CaCO_3$

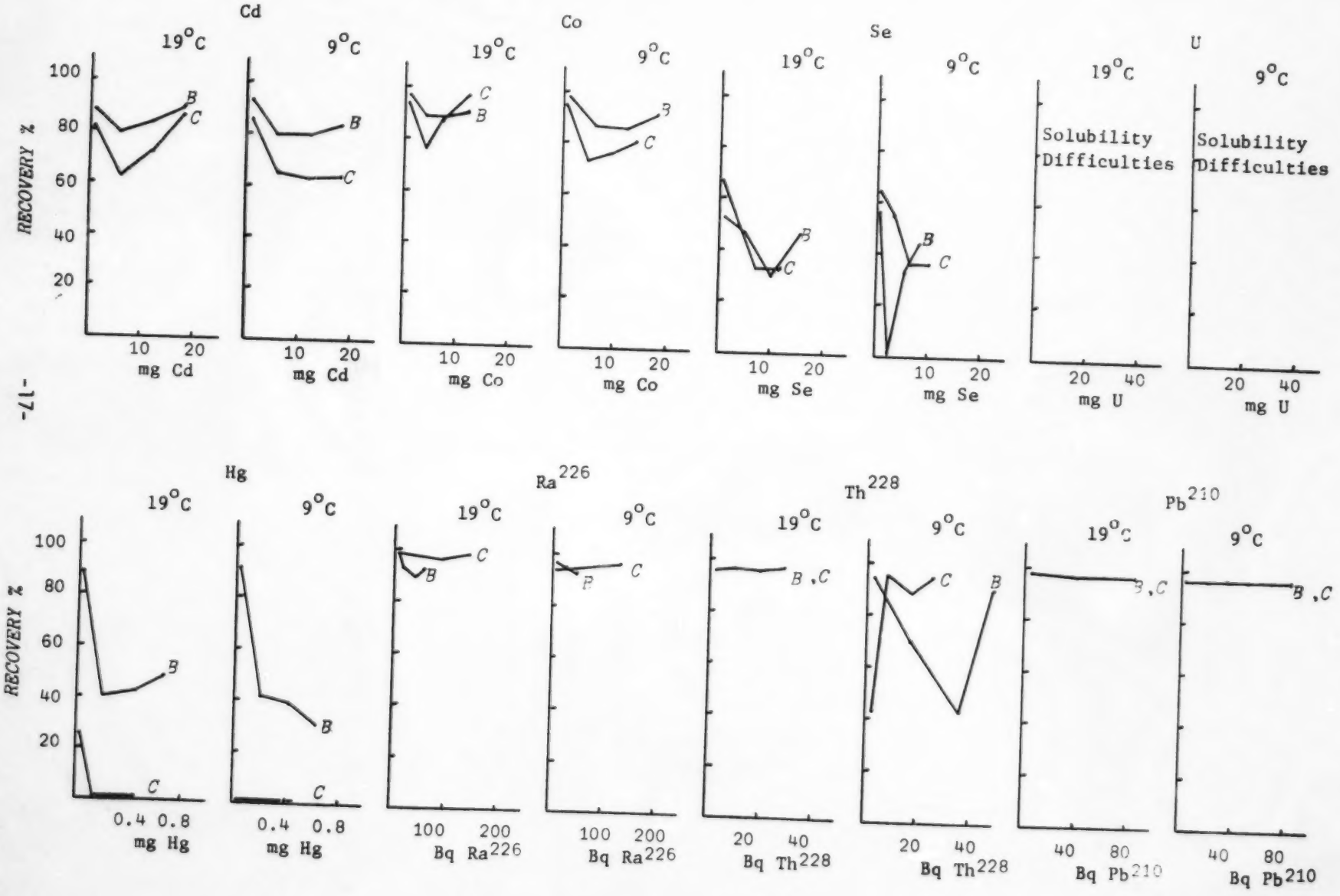


TABLE 3

BEHAVIOUR OF MnO_2/ACRYLIC FIBRE FILTER AS A FUNCTION OF SOLUTION HARDNESS AT pH LEVELS OF 4 AND 9, AND TEMPERATURE OF 19°C.

pH	Hardness mg/L $CaCO_3$	Volume, Elution, Litre	Cd mg/L	Co mg/L	Se mg/L	U mg/L	Hg mg/L	Ra-226 BQ/L	Th-228 BQ/L	Pb-210 BQ/L	Ca mg/L
4	200	Start Sol'n	1.40	1.15	1.0	2.1	0.052	7.8±0.1	1.7±0.1	5.1±0.4	61
		1	0.02 (99)	0.01 (99)	0.4 (60)	0.3 (86)	0.014 (83)	0.14±0.01 (98)	0.96±0.09 (44)	<1.	32
		6	0.45 (68)	0.36 (69)	0.6 (40)	0.8 (62)	0.061 (0)	0.17±0.03 (98)	0.88±0.11 (48)	<1.	64
		12	0.56 (60)	0.47 (59)	0.5 (50)	1.3 (38)	0.060 (0)	0.23±0.04 (97)	0.70±0.08 (59)	<1.	64
		18	0.64 (54)	0.54 (53)	0.5 (50)	1.6 (24)	0.057 (0)	0.18±0.04 (98)	1.3±0.1 (24)	<1.	62
		Start Sol'n	0.96	0.68	1.7	≤0.1	0.037	3.2±0.1	1.6±0.1	4.5±0.3	62
9	200	1	0.12 (87)	0.02 (97)	0.8 (53)	≤0.1	0.004 (89)	≤0.05 (99)	0.06±0.02 (96)	<1.	31
		6	0.20 (79)	0.08 (88)	0.9 (47)	≤0.1	0.022 (41)	0.19±0.01 (94)	0.05±0.01 (97)	<1.	61
		12	0.16 (83)	0.08 (88)	1.2 (30)	≤0.1	0.021 (43)	0.32±0.02 (90)	0.06±0.02 (96)	<1.	62
		18	0.11 (89)	0.06 (91)	0.9 (47)	≤0.1	0.019 (49)	0.23±0.03 (93)	≤0.05 (97)	<1.	63
		Start Sol'n	1.31	1.09	0.8	2.0	0.052	8.1±0.4	1.5±0.3	6.5±0.5	309
4	1000	1	0.19 (85)	0.13 (88)	≤0.4	0.28 (86)	0.043 (17)	0.19±0.03 (98)	1.2±0.1 (23)	<1.	258
		6	0.85 (35)	0.57 (48)	≤0.4	1.24 (38)	0.061 (0)	0.39±0.05 (95)	1.1±0.1 (30)	<1.	297
		12	0.90 (31)	0.61 (44)	0.4 (50)	1.61 (20)	0.055 (0)	0.45±0.06 (94)	1.1±0.1 (30)	<1.	302
		18	0.97 (20)	0.67 (39)	0.6 (25)	1.68 (16)	0.056 (0)	0.24±0.06 (97)	1.3±0.1 (13)	<1.	299
		Start Sol'n	0.98	0.62	1.2	≤0.1	0.019	7.9±0.3	2.0±0.2	8.0±1.0	301
9	1000	1	0.19 (81)	0.04 (94)	≤0.4 (67)	≤0.1	0.014 (26)	≤0.05 (99)	≤0.05 (97)	<1.	259
		6	0.39 (60)	0.15 (76)	0.6 (50)	≤0.1	0.036 (0)	0.49±0.08 (94)	≤0.05 (97)	<1.	300
		12	0.27 (72)	0.08 (87)	0.8 (33)	≤0.1	0.033 (0)	0.20±0.05 (97)	≤0.05 (97)	<1.	301
		18	0.13 (87)	0.02 (97)	0.8 (33)	≤0.1	0.035 (0)	≤0.05 (99)	≤0.05 (97)	<1.	296

TABLE 4 BEHAVIOUR OF MnO_2/ACRYLIC FIBRE FILTER AS A FUNCTION OF SOLUTION HARDNESS AT pH LEVELS OF 4 AND 9, AND TEMPERATURE OF 9°C.

pH	Hardness mg/L $CaCO_3$	Volume, Elution, Litre	Cd mg/L	Co mg/L	Se mg/L	U mg/L	Hg mg/L	Ra-226 BQ/L	Th-228 BQ/L	Pb-210 BQ/L	Ca mg/L
4	200	Start Sol'n	1.41	1.14	1.7	1.7	0.050	7.3±0.3	1.3±0.1	3.7±0.3	63
		1	0.02 (99)	0.02 (98)	0.6 (65)	≤0.1 (94)	0.014 (72)	0.25±0.04 (97)	0.92±0.09 (29)	≤1.	35
		6	0.48 (66)	0.43 (62)	0.9 (47)	0.5 (71)	0.058 (0)	0.32±0.05 (96)	0.81±0.09 (38)	≤1.	63
		12	0.67 (52)	0.53 (54)	1.0 (41)	1.0 (41)	0.061 (0)	0.23±0.03 (97)	1.02±0.10 (22)	≤1.	64
		18	0.72 (49)	0.60 (47)	1.0 (41)	1.2 (29)	0.056 (0)	0.22±0.03 (97)	0.71±0.07 (45)	≤1.	64
9	200	Start Sol'n	1.00	0.96	0.9	0.21	0.036	2.3±0.2	3.0±0.1	2.0±0.2	62
		1	0.08 (92)	0.02 (98)	≤0.4 (56)	≤0.1 (52)	0.003 (92)	≤0.05 (98)	0.08±0.03 (97)	≤1.	29
		6	0.21 (79)	0.12 (87)	1.3 (0)	≤0.1 (52)	0.021 (42)	0.26±0.01 (89)	0.91±0.08 (70)	≤1.	60
		12	0.21 (79)	0.13 (86)	0.6 (34)	≤0.1 (52)	0.022 (39)	0.25±0.05 (89)	1.7±0.1 (43)	≤1.	61
		18	0.15 (85)	0.08 (92)	0.5 (44)	0.15 (29)	0.025 (31)	0.13±0.03 (94)	0.017±0.002 (99)	≤1.	61
4	1000	Start Sol'n	1.33	1.02	0.4	2.1	0.048	8.0±0.5	1.62±0.06	6.5±0.5	297
		1	0.22 (83)	0.17 (83)	≤0.4	0.5 (76)	0.041 (15)	0.10±0.04 (99)	1.6±0.1 (0)	≤1.	269
		6	1.00 (25)	0.73 (28)	0.6	1.7 (19)	0.055 (0)	1.9±0.02 (76)	1.30±0.03 (19)	≤1.	293
		12	1.07 (20)	0.77 (25)	0.6	1.9 (10)	0.053 (0)	1.5±0.1 (81)	1.08±0.03 (32)	≤1.	294
		18	1.11 (17)	0.81 (21)	0.8	1.9 (10)	0.050 (0)	1.7±0.1 (79)	1.05±0.03 (33)	≤1.	296
9	1000	Start Sol'n	1.09	0.78	1.1	≤0.1	0.021	7.2±0.3	1.4±0.1	1.6±0.3	300
		1	0.16 (85)	0.04 (95)	0.4 (64)	≤0.1 (0)	0.020 (0)	0.11±0.03 (98)	0.8±0.4 (43)	1.2±0.2	260
		6	0.40 (63)	0.21 (73)	0.5 (55)	≤0.1 (0)	0.039 (0)	0.23±0.06 (97)	≤0.05 (96)	≤1.	300
		12	0.41 (62)	0.19 (76)	0.7 (36)	≤0.1 (0)	0.036 (0)	0.31±0.07 (96)	0.16±0.04 (89)	≤1.	289
		18	0.40 (63)	0.14 (82)	0.7 (36)	≤0.1 (0)	0.038 (0)	0.06±0.01 (99)	0.07±0.04 (95)	≤1.	297

3.3.3 Task C and Task D - Evaluation of Pump Feed and Gravity Feed

The application of the manganese dioxide/acrylic fiber filter to field sampling requires that a practical means of sample introduction be used. The two obvious possibilities are firstly gravity feed from a batch collected sample and secondly, hand pumping the liquid directly from the field location. These two options were evaluated with a view toward assessing the possible influence of flow rate on the recovery efficiency of the filters. Four experiments were carried out in which 18 liters of solution were passed through four identical filters:

(1) hand pump introduction at 2 liters/min
(2) gravity feed introduction at 0.4 liters/min
(3) gravity feed introduction at 1.6 liters/min
(4) gravity feed introduction at 2 liters/min

The results of the experiments are shown in Table 5. Figure 5 illustrates the removal efficiency of the filter as a function of the amount of each element elated at flow rates 0.4, 1.6 and 2.0 liters/min. Because of the design limititations, it was found virtually impossible to produce flow rates greater than 2 liters/min. In general, a small influence of flow rate is indicated. The efficiencies at 0.4 liter/min are , generally speaking, about 10% higher than at 1.6 and 2.0 liters/min. All the results illustrated in Figure 5 were obtained using gravity feed.

As expected, the removal efficiencies observed with the hand pump system (2 liters/min) was very similar to the gravity feed system results. However, in terms of practicality it has several disadvantages:

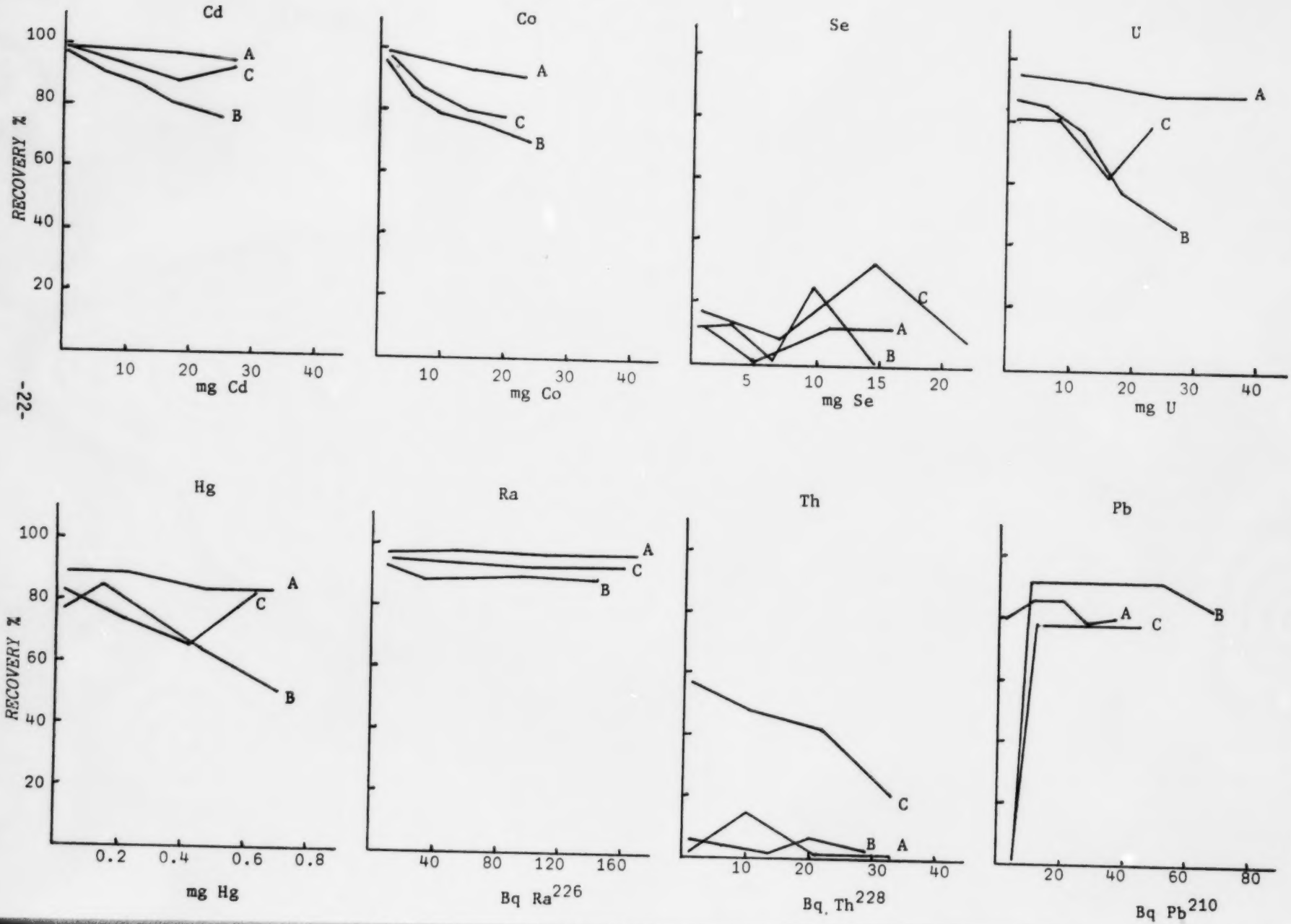
(1) it requires constant attention. With the gravity feed system no attention is needed during filtration
(2) It is a mechanical device, with moving parts. As such, it is prone to malfunction which can be intolerable in field sampling situations.

TABLE 5

INFLUENCE OF PUMP VERSUS GRAVITY FLOW, T = 19°C, pH = 4, HARDNESS = 0

Mode	Elution, Volume, Litres	Cd mg/L	Co mg/L	Se mg/L	U mg/L	Hg mg/L	Ra-226 Bq/L	Th-228 Bq/L	Pb-210 Bq/L
Handpump,	Start	1.44 --	1.6 --	1.0 --	1.43 --	0.038	8.7±0.4	0.89±0.09 --	2.6±0.2
Flow=2L/min.	1	0.04 (97)	0.04 (97)	1.0 (0)	0.32 (78)	0.019 (50)	0.72±0.09 (92)	0.65±0.08 (27)	--
pH=4	2	--	--	--	--	--	--	--	<0.3 (89)
T=18°C.	4	0.12 (92)	0.17 (89)	1.0 (0)	0.22 (85)	0.012 (68)	0.54±0.08 (94)	0.68±0.09 (24)	--
	5	--	--	--	--	--	--	--	<0.3 (89)
	8	0.18 (87)	0.17 (89)	1.0 (0)	0.41 (71)	0.012 (68)	0.61±0.06 (93)	0.64±0.08 (28)	--
	9	--	--	--	--	--	--	--	<0.3 (89)
	12	0.23 (84)	0.23 (86)	1.0 (0)	0.47 (67)	0.012 (68)	0.73±0.10 (92)	0.58±0.07 (35)	--
	13	--	--	--	--	--	--	--	--
	17	--	--	--	--	--	--	--	--
	18	0.24 (83)	0.25 (84)	1.0 (0)	0.47 (67)	0.014 (63)	0.42±0.09 (95)	0.72±0.09 (19)	0.50±0.05 (81)
Gravity Feed	Start	1.40 --	1.31 --	0.8 --	1.49 --	0.039	8.0±0.3 --	1.63±0.15	4.0±0.2
Flow=1.6L/min.	1	0.04 (97)	0.05 (96)	0.7 (12)	0.19 (87)	0.009 (77)	0.58±0.05 (93)	1.53±0.12 (6)	--
pH=4	2	--	--	--	--	--	--	--	5.4±0.2 (0)
T=18°C.	4	0.12 (91)	0.20 (85)	0.7 (12)	0.23 (85)	0.006 (85)	0.85±0.05 (89)	1.56±0.14 (4)	--
	5	--	--	--	--	--	--	--	<0.3 (92)
	8	0.21 (85)	0.28 (79)	0.8 (0)	0.49 (67)	0.010 (74)	0.85±0.05 (89)	1.61±0.14 (1)	--
	9	--	--	--	--	--	--	--	<0.3 (92)
	12	0.27 (81)	0.32 (76)	0.6 (25)	0.62 (58)	0.014 (64)	0.79±0.12 (90)	1.51±0.15 (7)	--
	13	--	--	--	--	--	--	--	<0.3 (92)
	17	--	--	--	--	--	--	--	0.68±0.06 (83)
	18	0.33 (76)	0.39 (70)	0.8 (0)	0.81 (46)	0.019 (51)	0.90±0.06 (89)	1.59±0.12 (2)	--
Gravity Feed	Start	1.47	1.14	1.2	1.30	0.035	8.7±0.5	1.82±0.14	2.6±0.1
Flow=2L/min.	1	0.03 (98)	0.02 (98)	1.0 (17)	0.25 (81)	0.006 (83)	0.47±0.03 (95)	0.96±0.11 (47)	--
pH=4	2	--	--	--	--	--	--	--	2.7±0.1 (0)
T=18°C.	5	--	--	--	--	--	--	--	<0.3 (88)
	6	0.09 (94)	0.15 (87)	1.1 (8)	0.26 (80)	0.009 (74)	0.54±0.10 (94)	0.94±0.12 (48)	--
	9	--	--	--	--	--	--	--	<0.3 (85)
	12	0.18 (88)	0.23 (80)	0.8 (33)	0.51 (61)	0.012 (66)	0.59±0.04 (93)	1.05±0.10 (42)	--
	13	--	--	--	--	--	--	--	<0.3 (88)
	17	--	--	--	--	--	--	--	<0.3 (88)
	18	0.11 (93)	0.14 (88)	1.1 (8)	0.27 (79)	0.006 (83)	0.59±0.11 (93)	1.43±0.13 (21)	--
Gravity Feed	Start	1.48	1.27	0.9	2.12	0.038	9.3±0.3	1.82±0.17	2.2±0.1
Flow=0.4L/min.	1	0.01 (99)	0.01 (99)	0.8 (12)	<0.10 (95)	0.004 (89)	0.30±0.06 (97)	1.81±0.19 (13)	--
pH=4	2	--	--	--	--	--	--	--	0.44±0.04 (80)
T=18°C.	5	--	--	--	--	--	--	--	<0.3 (86)
	6	0.03 (98)	0.04 (97)	1.0 (0)	0.14 (93)	0.004 (89)	0.20±0.02 (98)	1.54±0.14 (15)	--
	9	--	--	--	--	--	--	--	<0.3 (86)
	12	0.05 (97)	0.09 (93)	0.8 (17)	0.23 (89)	0.006 (84)	0.25±0.07 (97)	1.8±0.2 (0)	--
	13	--	--	--	--	--	--	--	0.49±0.05 (78)
	17	--	--	--	--	--	--	--	0.45±0.05 (80)
	18	0.09 (95)	0.12 (91)	0.8 (12)	0.24 (89)	0.006 (84)	0.30±0.06 (97)	1.8±0.2 (0)	--

FIGURE 5 - Influence of Flow Rate on the Removal Efficiency of the MnO_2 Filter. Temp.=19°C, pH=4.0, Hardness=0 mg/$CaCO_3$. A, 0.4 L/min; B, 1.6 L/min; C, 2.0 L/min.



3.3.4 Task E - Evaluation of Desorption Techniques

The application of the manganese dioxide filter as a sampling device requires that the adsorbed elements be removed for quantification. In this task, six of the filters used in tasks A to D were choosen. The individual packings from three were soaked in 50 milliliters nitric acid and the other three packings were soaked in 50 milliliters of 10% hydroxylamine hydrochloride. After one hour the solution/filter mixtures were filtered,washed and made up to 200 millilliter volume. These solutions were analysed for Cd, Cu, Se, Hg, U, Ra-226, Th-228 and Pb-210 contents. The results, expressed as mg/filter (Bq/filter for Ra-226, Th-228 and Pb-210) are shown in Table 6. Corrections for inherent impurities naturally present in the filter materials were made by subjecting unused filters to the same extraction processes.

The description of the filters choosen are as follows:

filter 1	see Table 5; gravity feed, flow 1.6 L/min; pH 4, T = 18 degrees C
filter 2	see Table 5; handpump feed, flow 2. L/min; pH4, T = 18 degrees C
filter 3	see Table 3; pH 9, hardness 200 mg/L CaCO3
filter 4	see Table 5; gravity feed, 2.0 L/min, pH 4, T = 18 degrees C
filter 5	see Table 5; gravity feed, 0.4 L/min, pH 4, T = 18 degrees C
filter 6	see Table 4, pH 4, hardness 200 mg/L CaCO3.

Eighteen liters of solution had been eluted through each of the 6 filters. The theoretical amounts adsorbed of each filter was based on the composition of the solutions prior to and after filtration.

Table 6 shows that desorption with nitric acid is not totally effective in removing all the cations known to be present on the manganese dioxide filters. While it appeared to be effective for desorbing Cd, Hg and Pb-210 it did not give good recovery for Co, Se, U, Ra-226 and Th-228. The use of hydroxylamine hydrochloride as a desorber was much more effective for Cd, Co, Se, U, Ra-226, Th-228 and Pb-210. One possible explanation for the better effectiveness of hydroxylamine is that it dissolves the manganese dioxide, hence "freeing" any cations trapped in the crystal structure. With nitric acid a desorption mechanism similar to ion exchange may be taking place. As a result those cations trapped in the crystal structure were not removed.

TABLE 6: Composition of Eluants resulting from Desorption Experiments Using Nitric Acid and Hydroxylamine Hydrochloride. Numbers in brackets are theoretical contents of filters based on calculation from earlier experiments.

Filter No.	Extractant	mg					Bq		
		Cd	Co	Se	Hg	U	Ra-226	Th-228	Pb-210
1.	HNO_3	15 (25)	18 (22)	0.5 (0.7)	0.7 (0.6)	13 (24)	25 (137)	0.7 (12)	47 (58)
2.	HNO_3	15 (22)	15 (24)	0 (0.0)	0.5 (0.4)	11 (18)	7 (144)	3.0 (4)	59 (42)
3.	HNO_3	17 (14)	6 (11)	5 (14)	0 (0)	-	22 (54)	0.5 (27)	100 (81)
4.	Amine	17 (24)	15 (17)	2 (3)	≤0.1 (0.4)	-	148 (145)	12 (13)	31 (37)
5.	Amine	22 (25)	20 (21)	2 (1.6)	≤0.1 (0.5)	30 (34)	169 (162)	2 (1.6)	36 (32)
6.	Amine	14 (14)	10 (11)	10 (12)	≤0.1 (0.2)	12 (15)	132 (127)	6 (7)	80 (66)

3.3.5 Task F- Influence of dissolved Iron Content on the Removal of Ra-226 from Solution using the Manganese Dioxide Filter

The terms of the contract for this project included the requirement that the influence of iron on the efficiency of radium-226 removal by the manganese dioxide filter be examined. Three solutions,each containing approximately 7 Bq/L radium-226 and 0.01mg/L, 0.1 mg/L and 1.0 mg/L iron , respectively , were prepared. Twenty litres of each were then passed through individual manganese dioxide filters. The effluent from each filter was collected. Analyses for radium-226 were made on the ninth and eighteenth litre eluted from each filter. The results, tabulated in Table 7 , show that in all three experiments the radium -226 content of the effluents were more than 95% reduced by the manganese filter. Under the conditions of these experiments , the presence of dissolved iron in concentrations ranging from 0.01 to1.0 mg/L had no significant influence on filter performance. This observation does not necessarily imply that the presence of dissolved iron will not effect the capacity of the filter for radium-226. However, it does imply that the filter has a capacity for radium-226 that exceeds 100 Bq when as much as 1. mg/L dissolved iron is present in the solution to be treated.

TABLE 7

INFLUENCE OF DISSOLVED IRON
ON THE REMOVAL EFFICIENCY OF THE
MANGANESE FILTER FOR RADIUM-226

Elution Volume, Litre	Ra-226 BQ/L	Removal Efficiency, %
0.01 ppm Iron		
Start	7.9±0.1	--
9	0.18±0.02	98
18	0.12±0.01	98
0.1 ppm Iron		
Start	6.4±0.2	--
9	0.22±0.02	97
18	0.04±0.01	99
1.0 ppm Iron		
Start	7.3±0.3	--
9	0.39±0.02	95
18	0.28±0.02	96

IV CONCLUSIONS AND RECOMMENDATIONS OF LABORATORY PROGRAM

As a result of the phase I laboratory study several conclusions are possible:

1. The best substrate , for use in preparing the manganese filter , is acrylic fiber.

2. There is an apparent pH effect and hardness effect that must be considered when attempting to use the filter as a sample device. For the elements Cd, Co, and Hg the pH of the solution must be greater than 3.0 in order to ensure greater than 80% removal efficiency. As the hardness increased to greater then 200 mg/L CaCO3 the efficiency and capacity decreased to less than 50%.

3. The removal of radium-226 from solution is not influenced by pH or hardness. Removal efficiences of greater then 90% were observed in all experiments.

4. The presence of iron in concentrations as high as 1.0 mg/L does not adversely affect the attractiveness of the filter toward radium-226.

5. Thorium removal appears to be most effective at low pH levels.

6. The behaviour of Pb-210 appears to be similar to that of Ra-226 at low pH levels of ~4 and high pH levels of ~9. However at intermediate pH levels there is indication of loss of filter efficiency and capacity.

7. The behaviour of the filter at temperatures of 19 degrees C and 9 degrees C was judged to be very similar.

8. The slower the flow rate through the filter the better the removal efficiencies .For radium-226 a flow rate of 0.4 liters/min gave a removal efficiency of 98% while with a flow rate of 2 liters/min the removal efficiency was 90%.

In summary, the primary recommendation of the laboratory program is that manganese dioxide impregnated on acrylic fiber is an excellent device for concentrating radium-226 from large volumes of synthetic water samples. Its beheviour toward radium-226 was not found to be influenced by pH or solution hardness. The removal efficiency for radium-226 was excellent at solution temperatures between 10 degrees C to 20 degrees C. As a result it is suggested that this filter has a very high commercial potential as a sampling technique for, at least, radium-226. Consequently, it was recommended that phase II of the proposal, involving field testing of actual "real life" samples, be conducted.

V- FIELD EVALUATION

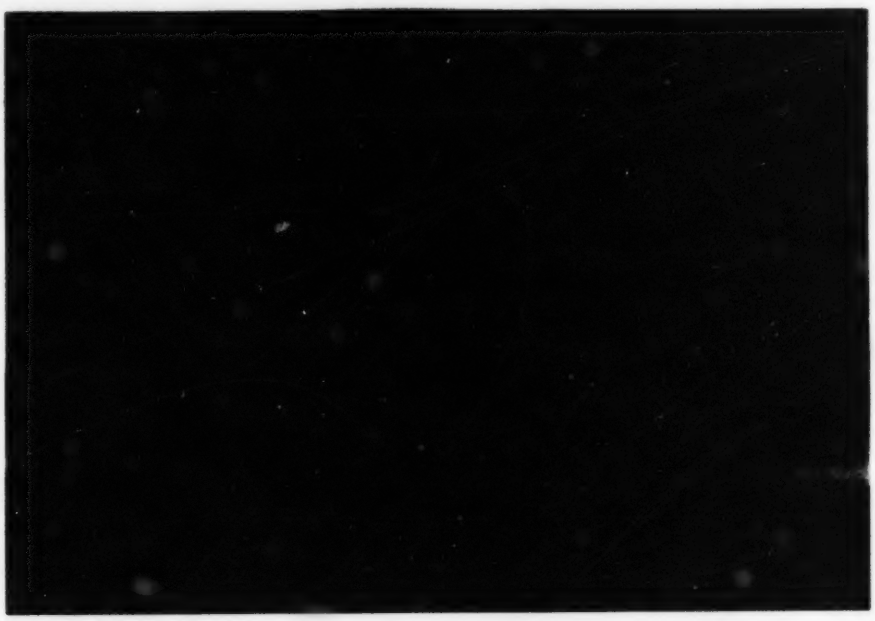
5.1 Field Procedure

As a result of the findings of the laboratory evaluation (Phase I) it was decided that Phase II, the field testing portion of the project, be done. The cooperation of two Saskatchewan Uranium Mining and Drilling companies, Amok Limited and Eldor Mines Limited , was solicited and their approval was received. As a consequence, a field team was sent to the Rabbit Lake mine site of Eldor Mines Limited. The procedure for field evaluation was as follows:

1) Five sites were chosen for sampling. Each had pH's between 5.0 and 7.5.
2) At each location a 20 litre grab sample of water was taken in a plastic container (Canadian Tire - 20 liter water container). A manganese filter cassett, described in Section 3.1, was attached to it, and the water allowed to flow through the filter by gravity (flow rate of 0.5 liters/min). After complete elution of the 20 liters, the filter cassette was detached from the plastic container and packaged for transport to the Monenco laboratory. The sampling equipment is shown in the photograph below.
3) A two liter sample of water was then collected in a two liter plastic bottle, and preserved by the addition of 20 ml. of concentrated nitric acid. This sample was also returned, along with the filter from Step (2) to the laboratory for analysis
(4) Steps (2) and (3) were repeated at the four other sampling sites.
(5) At all five sampling sites, Step (2) was carried out in duplicate.
(6) In all cases, the sampling was assisted and witnessed by Eldor Mines Ltd. Environmental department personnel.

At the Amok Limited, Cluff Lake site the sampling and grab sample analyses were the responsibility of Amok personnel. A Monenco field team was not present during the sampling. After sampling, at the two sites, the manganese filter cassettes were sent to Monenco for analyses.

Upon arrival at the Monenco radiochemistry laboratory, the grab samples were analysed for U, Ra-226, Pb-210, Cd, Co, Fe and Se using the methodologies described in Section 3.2. The manganese dioxide packing from each filter cassette was removed and the adsorbed contents removed using 10% hydroxylamine hydrochloride as described in Section 3.3.4. The resulting extracts, representing the contents of 20 liters of filtered field sample, were then analysed for U, Ra-226, Pb-210, Cd, Co, Fe and Se using methodologies described



Photograph 2 - Photo of Field Sampling Equipment

in Section 3.2. The results were expressed in units of Becquerels (and milligrams) per liter of filtered sample.

5.2 Results and Discussions

Table 8 is a summary of the results. It shows a comparison between data obtained from analysis of the grab samples and those obtained from analysis of the manganese dioxide filters.

For the most part, the data contained in table 8 show that the solutions selected for field testing contained concentrations of Pb-210, Cd, Co and Se that were lower than the detection limits of the instrumentation used. The application of the manganese dioxide sampling device allowed those detection limits to be improved considerably. The concentrations of uranium and radium-226 were significant at each site and ,as a consequence ,good agreements were obtained between analyses of grab samples and analyses by application of the manganese sampling device. With uranium, good agreement was obtained for four of the five sites. For radium-226 the agreement appeared to be not as good as expected ,based upon the laboratory experimental results. That is, some of the results obtained by grab sampling were significantly higher than the results obtained after application of the sampling device. The most probable explaination for this is related to the difference between "total" metal content and "dissolved" metal content. The grab sample analyses represent "total" radium content and the manganese filter results represent "dissolved" radium content. In order to have measured the "dissolved" radium content, filtration of the grab sample prior to preservation would have been necessary. The manganese sampling device is not designed to remove suspended matter but to adsorb "dissolved" radium. In addition ,there is sufficient evidence available from the mining company that confirms that, at the sample sites in question, a significant portion of the "total" radium-226 is present in both the "suspended" and the "dissolved" forms.

TABLE 8

COMPARISON OF ANALYSIS VIA GRAB SAMPLING MODE (G) WITH ANALYSIS BY FILTRATION USING THE MANGANESE DIOXIDE FILTER (M). *The G Mode Represents "Total" Cations and the M Mode Represents "Dissolved" Cations. Number in Brackets Represent Duplicate Values

Location No.	Description	Sampling Mode *	U, µg/L	Ra-226 BQ/L	Pb-210 BQ/L	Cd mg/L	Co mg/L	Se mg/L
1	Hidden Bay Aug. 7	G	1.0	0.018±0.016	0.7	≤0.003	≤0.006	≤0.6
		M	0.8	0.0080±0.0001 (0.0070±0.0002)	≤0.04	≤0.00002	≤0.00005	≤0.008
2	South Tailing Pond - Aug. 7	G	340.0	1.3±0.1	≤0.70	≤0.003	≤0.006	≤0.6
		M	371.0	0.285±0.014 (0.255±0.005)	≤0.04	≤0.00002	0.0014±0.0001	≤0.008
3	Hidden Bay Effluent	G	30.	0.022±0.015	≤0.7	≤0.003	≤0.006	0.6
		M	25.	0.0070±0.0001 (0.052±0.006)	≤0.04	≤0.00002	0.0020 ±0.0001	≤0.008
4	Collins Bay	G	≤0.5	≤0.005	≤0.7	≤0.003	≤0.006	≤0.6
		M	0.27±0.01	0.0003±0.0001 (0.0008±0.0002)	≤0.04	≤0.00002	0.00010 ±0.0005	≤0.008
5	Tailing Pond Pumphouse	G	790.0	2.9 ±0.1	≤0.7	≤0.003	≤0.006	≤0.6
		M	209.0	0.700±0.005 (0.705±0.005)	0.13±0.01	≤0.00002	0.00200± 0.0001	0.067±0.002
6	Amok - Solid Pond	G	--	30.	--	--	--	--
		M	--	23. ±1.	0.220±0.010	--	--	--
7	Amok - STS	G	--	0.02	--	--	--	--
		M	--	0.019±0.003	0.050±0.005	--	--	--

VI FIELD PROGRAM CONCLUSIONS AND RECOMMENDATIONS

For the most part the results of the field program support the finding of the laboratory experimental program. Due to the larger effective sample size that it represents, the field sampling procedure is shown to give a factor of 20 to 30 times greater sensitivity than the standard grab sampling procedure.

One feature of the manganese dioxide field sampling device is that it appears to remove only "dissolved" cations from solution. It is not designed to filter out solid, small diameter particles which may themselves be carrying adsorbed cations. Consequently comparison with "total" and "extractable" metal contents of some field solutions may often reveal that the manganese filter results are lower by a significant amount. Under the terms of the project, this feature has not been fully demonstrated. Further field evaluation is necessary if it is to be confirmed.

It is recommended that the field portion of this study be extented to include detailed sampling at 50 or more locations. The objectives of the program should be as follows:

1. Determine the distribution of "dissolved" and "undissolved" radium-226 at selected locations.

2. Confirm the efficiency of the manganese dioxide device to adsorb "dissolved" and "undissolved" radium-226.

3. Demonstrate, in greater detail and under more varying conditions, the advantages of the field sampling device.

VII - PROJECT SUMMARY

The most significant finding of this project is that dissolved radium-226 can be adsorbed on a field sampling device with an efficiency (greater than 90%) that is relatively independent of pH and solution hardness. In addition, the capacity of the device for radium-226 has been shown to be greater than 100 Becquerels. While the filter has also been shown to have attractiveness, for certain other dissolved cations, variables, such as pH and solution hardness appear to influence the efficiency of their removal. As a result, it is envisaged that this field sampling device has very good commercial value as a means of analysing for dissolved radium-226 in remote areas of the world. It is proposed that a

canadian commercial Laboratory operation would provide the filter to regulatory agencies who would pass a large volume of the desired aqueous sample through it. Upon completion the filtered device would be sealed tightly and returned to the laboratory for analysis. Since radium-226 emanates radon-222 (half-life of 3.8 days) it would be necessary to allow 20 days for secular equilibrium between the two to be achieved. At that time the radium-226 could be determined using gamma spectroscopy by measuring the gamma emitting daughter bismuth-214. In summary the advantages of such a device for field sampling are as follows:

1. The sensitivity over that of the presently used grab sampling techniques would be greater.

2. Field preservation with dangerous acids would not be necessary. This would considerably reduce one of the major difficulties now associated with radium-226 monitoring.

3. The cost of analysis would be considerably reduced. In addition to not requiring acid for preservation the weight of sample returned to the laboratory would be of the order of 20 grams rather than 20 kilograms required for equivalent sensitivity by grab sampling. Once received by the laboratory the cost of analysis would be reduced by a factor of 20-30% over the current analysis fee rates. This would be due primarily to the use of gamma spectroscopy as the analysis technique. The use of gamma spectroscopy would reduce the manpower requirements now required for the wet chemistry based alpha spectrometric or radon emanation now in common use when relatively small sample volumes are available.

4. The reduced cost and increased ease of sampling would allow more comprehensive radium-226 monitoring programs to be carried out.

5. The patenting of such a field sampling device could lead to the creation of a new Canadian commercial venture that would have good export potential.

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